

# PATENT ABSTRACTS OF JAPAN

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(71)Applicant : **mitsubishi heavy ind  
LTD**

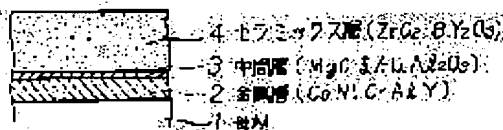
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(72)Inventor : **KAWAI HISATAKA**  
**IMAZU TAKAYUKI**  
**KANIKAWA MASAYA**  
**KITAI TAKAHITO**  
**HIROTA NORIHIDE**

**(54) COATING FILM FOR HEAT SHIELDING**

(57)Abstract:

**PURPOSE:** To provide the long-life coating film for heat shielding having high oxidation preventing performance and excellent peeling resistance by hating by successively laminating and forming a metallic layer and a ceramic layer in tight contact via a dense intermediate layer on the surface of a base material.



**CONSTITUTION:** The coating film for heat shielding consisting in tight contact of the laminated films is formed by successively providing the surface of the base material 1, such as heat resistant alloy, with the metallic layer 2 having the high corrosion resistance and oxidation resistance, the dense intermediate layer 3 having no oxygen conductivity and the ceramic layer 4 having excellent heat shieldability. MCrAlY (M is Ni, Co, Fe, etc.) is used as the metallic layer 2, MgO, Cab, CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc., are used as the intermediate layer 3 and ZrO<sub>2</sub>, systems, such as ZrO<sub>2</sub>.MgO,

ZrO<sub>2</sub>.Y<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>.CeO<sub>2</sub>, as the ceramic layer. The respective layers of the laminated films are coated by a plasma thermal spraying method, physical vapor deposition method by electron beams, etc.

## CLAIMS

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### [Claim(s)]

[Claim 1] Thermal-barrier-coating film characterized by consisting of a ceramic layer which is the cascade screen which it comes to prepare on a base material front face by carrying out sequential adhesion, and is rich in the high metal layer, the middle class who is precise and does not have oxygen conductivity, and thermal insulation nature of anticorrosion and oxidation resistance from a base material side.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the thermal-barrier-coating film especially applied in favor of turbine \*\*, stationary blade, and combustor (the container liner, tail pipe) of a gas turbine about the thermal-barrier-coating film.

[0002]

[Description of the Prior Art] The thermal-barrier-coating film for gas turbine elevated-temperature components (a turbine bucket and a stationary blade, combustor) by the conventional technique has structure as shown in drawing 2 and drawing 3 . That is, as are shown in drawing 2 , and the laminating of the metal layer 2 and the ceramic layer 4 is carried out to the base material 1 or it is shown in drawing 3 , it is the multilayer structure by which the metal layer 2, the metal-ceramic mixing layer 5, and the ceramic layer 4 were formed in the base material 1. The outermost layer of drum consists of a ceramic layer 4 also in which thermal-barrier-coating film.

[0003] In such thermal barrier coating, the metal layer 2 is for mainly making small the difference of the coefficient of thermal expansion of a base material 1, the ceramic layer 4, or the base material 1 and the metal ceramic mixing layer 5, and this aiming at relaxation of thermal stress, and preventing exfoliation of the ceramic layer 4. Moreover, the role rate of the metal layer 2 is aimed at much more positively also about the metal-ceramic mixing layer 5. In addition, generally the MCrAlY alloy system (element more than kinds, such as M:nickel, and Co, Fe) excellent in the anticorrosion and the oxidation resistance in an elevated temperature is used for this metal layer 2. Moreover, for the purpose of thermal insulation, thermal conductivity is low and the ceramic layer 4 is ZrO<sub>2</sub> with high emissivity. System ceramics (ZrO<sub>2</sub>, MgO, ZrO<sub>2</sub>, Y<sub>2</sub> O<sub>3</sub>, etc.) is mainly used.

[0004]

[Problem(s) to be Solved by the Invention] As for the gas turbine, elevated-temperature-ization of a turbine inlet gas temperature is progressing in recent years for efficient-izing. In connection with this, since the thermal-barrier-coating film is very effective in metal-temperature reduction of the elevated-temperature components of a gas turbine, also in gas turbine elevated-temperature components, it is applied to the turbine stationary blade severe in a service condition and combustor tail pipe other than a combustor container liner, and application to those with \*\*\*\* and a turbine bucket with a service condition severe further more is expected.

[0005] As a breakage gestalt of thermal barrier coating, the differential thermal expansion of the configuration layer of \*\* thermal barrier coating, and a base material, Exfoliation of the ceramic layer by the thermal stress resulting from a temperature gradient and \*\* metal layer are oxygen (generally a ceramic layer is porous). It expands by oxidation resulting from being exposed to an elevated temperature under the oxygen existence which has

passed this. There are corrosion of exfoliation near the ceramic layer of a metal layer, the metal layer by \*\* corrosive components (S, Na, V, etc.), and a ceramic layer and consumption of the ceramic layer by the erosion resulting from \*\* coming-flying particle. The breakage gestalt of the thermal barrier coating from which the thermal load which thermal barrier coating receives becomes high much more, and poses a problem most with elevated-temperature-izing of a turbine inlet gas temperature is above-mentioned \*\*. That is, although the metal layer excellent in oxidation resistance is used, in order that it may be exposed more to an elevated temperature under oxygen existence and a metal layer may oxidize, the problem that the life of \*\* and thermal barrier coating becomes [ this / a ream ] brief at exfoliation of a ceramic layer arises.

[0006] This invention tends to offer the thermal-barrier-coating film which solves this problem in view of an above-mentioned situation.

[0007]

[Means for Solving the Problem] This invention is a cascade screen which it comes to prepare on a base material front face by carrying out sequential adhesion, and it is the thermal-barrier-coating film characterized by consisting of a ceramic layer which is rich in anticorrosion, an oxidation-resistant high metal layer, the middle class that is precise and does not have oxygen conductivity, and thermal insulation nature from a base material side.

[0008] In this invention as a high metal layer of anticorrosion and oxidation resistance MCrAlY (element more than kinds, such as Y:nickel, and Co, Fe) It is precise and a coefficient of thermal expansion is the middle thing of said metal layer and the ceramic layer which is rich in the after-mentioned thermal insulation nature as an interlayer without oxygen conductivity. MgO, CaO, CeO<sub>2</sub>, and aluminum 2O<sub>3</sub> etc. -- moreover -- as the ceramic layer which is rich in thermal insulation nature -- ZrO<sub>2</sub>, MgO, ZrO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and CeO<sub>2</sub> etc. -- ZrO<sub>2</sub> The system ceramics is used.

[0009]

[Function] Since the interlayer who prevents trespass of oxygen exists in the medium, a metal layer does not oxidize, and exfoliation of the ceramic layer of an outermost layer of drum does not produce the thermal-barrier-coating film of this invention, but the life of the thermal-barrier-coating film becomes long.

[0010]

[Example] Drawing 1 R> 1 explains one example of the thermal-barrier-coating film of this invention. As shown in drawing 1, it has the multilayer structure by which the laminating of the high metal layer 2 of anticorrosion and oxidation resistance, the interlayer 3 who prevents trespass of oxygen, and the ceramic layer 4 with a thermal insulation property high as an outermost layer of drum was carried out in order on the base material 1.

[0011] In the thermal-spraying material for the metal layers 2, it is ZrO<sub>2</sub>-8Y<sub>2</sub>O<sub>3</sub> to the thermal-spraying material for ceramic layer 4 about CoNiCrAlY (Co-32nickel-21Cr-3aluminum-0.5Y). It used and MgO or aluminum 2O<sub>3</sub> was used for the thermal-spraying material or coating material for middle class 3.

[0012] Four kinds of test specimens shown in a table 1 were produced using above-mentioned thermal-spraying material or an above-mentioned coating material. First, sample It is aluminum 2O<sub>3</sub> about the front face of the heat-resistant alloy (Co radical alloy: 30x50x3mmt) which is a base material 1 in No.1. Grid blast processing was performed with the grain and the heat-resistant-alloy front face was changed into the condition of having been suitable for the plasma metal spray. Next, thermal spraying of the high metal layer of anticorrosion and oxidation resistance was carried out by the low voltage plasma metal spray method. Moreover, the middle class was coated with electron beam physical vapor deposition, and thermal spraying of the ceramic layer was carried out to the last by the atmospheric-air plasma metal spray approach. Sample Except for having carried out

thermal spraying of the interlayer by the low voltage plasma metal spray method in No.2 The test specimen was produced in the same way as No.1. Sample Except for having changed an interlayer's construction material in No.3 The test specimen was produced in the same way as No.1. Sample No.4 are the conventional thermal barrier coating and they were produced in the way same as comparison material as No.1. To the last, it is a sample. In order to raise the bond strength of the thermal barrier coating of No.1- No.4, 1000 degree-Cx 2 hours (heat treatment among a vacuum) were carried out as diffusion heat treatment.

[0013] The oxidation test by heating (1050 degree-Cx 300 hours) among an atmospheric-air electric furnace was carried out using the above-mentioned test specimen. It gazed at the cross-section microstructure after heating, and the oxidation resistance of a metal layer was evaluated. Next, the thermal cycling test (repetition between 950 degrees C and 200 degrees C) was carried out about front [ heating ] material and the material after heating (1050 degree-Cx 300 hours) among an atmospheric-air electric furnace. The number of heat cycles until exfoliation of a thermal-barrier-coating layer arises by the thermal cycling test estimated peeling resistance. These test results are shown in a table 2.

[0014] From a table 2, as compared with it of the former [ film / of this invention / thermal-barrier-coating ], there is little oxidation of a metal layer, and, for this reason, there were many numbers of cycles to exfoliation by the thermal cycling test of heating material, and the effectiveness of the thermal-barrier-coating film of this invention was proved.

[0015]

[A table 1]

\* APS Atmospheric-air plasma metal spray method LPPS Low voltage plasma metal spray method EB-PVD Electron beam physical vapor deposition [0016]

[A table 2]

[0017]

[Effect of the Invention] Since an interlayer is prepared between a ceramic layer and a metal layer and passage of oxygen is prevented by this interlayer, it is hard to produce oxidization of a metal layer, and the life of thermal-barrier-coating film of this invention of the thermal-barrier-coating film improves. Therefore, a severe operating environment with more high inlet gas temperature or the gas turbine elevated-temperature components (turbine \*\* and a stationary blade, a combustor container liner and a tail pipe) which are equal to a more nearly prolonged activity can be offered by applying the thermal-barrier-coating film by this invention to a gas turbine.

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## TECHNICAL FIELD

[Industrial Application] This invention relates to the thermal-barrier-coating film especially applied in favor of turbine \*\*, stationary blade, and combustor (the container liner, tail pipe) of a gas turbine about the thermal-barrier-coating film.

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## PRIOR ART

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[Description of the Prior Art] The thermal-barrier-coating film for gas turbine elevated-temperature components (a turbine bucket and a stationary blade, combustor) by the conventional technique has structure as shown in drawing 2 and drawing 3 . That is, as are shown in drawing 2 , and the laminating of the metal layer 2 and the ceramic layer 4 is carried out to the base material 1 or it is shown in drawing 3 , it is the multilayer structure by which the metal layer 2, the metal-ceramic mixing layer 5, and the ceramic layer 4 were formed in the base material 1. The outermost layer of drum consists of a ceramic layer 4 also in which thermal-barrier-coating film.

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## EFFECT OF THE INVENTION

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## TECHNICAL PROBLEM

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The breakage gestalt of the thermal barrier coating from which the thermal load which thermal barrier coating receives becomes high much more, and poses a problem most with elevated-temperature-izing of a turbine inlet gas temperature is above-mentioned \*\*. That is, although the metal layer excellent in oxidation resistance is used, in order that it may be exposed more to an elevated temperature under oxygen existence and a metal layer may oxidize, the problem that the life of \*\* and thermal barrier coating becomes [ this / a ream ] brief at exfoliation of a ceramic layer arises.

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## MEANS

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[Means for Solving the Problem] This invention is a cascade screen which it comes to prepare on a base material front face by carrying out sequential adhesion, and it is the thermal-barrier-coating film characterized by consisting of a ceramic layer which is rich in anticorrosion, an oxidation-resistant high metal layer, the middle class that is precise and does not have oxygen conductivity, and thermal insulation nature from a base material side.

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## OPERATION

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[Function] Since the interlayer who prevents trespass of oxygen exists in the medium, a metal layer does not oxidize, and exfoliation of the ceramic layer of an outermost layer of drum does not produce the thermal-barrier-coating film of this invention, but the life of the thermal-barrier-coating film becomes long.

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## EXAMPLE

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[Example] Drawing 1 R> 1 explains one example of the thermal-barrier-coating film of this invention. As shown in drawing 1 , it has the multilayer structure by which the laminating of the high metal layer 2 of anticorrosion and oxidation resistance, the interlayer 3 who prevents trespass of oxygen, and the ceramic layer 4 with a thermal insulation property high as an outermost layer of drum was carried out in order on the base material 1.

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with the grain and the heat-resistant-alloy front face was changed into the condition of having been suitable for the plasma metal spray. Next, thermal spraying of the high metal layer of anticorrosion and oxidation resistance was carried out by the low voltage plasma metal spray method. Moreover, the middle class was coated with electron beam physical vapor deposition, and thermal spraying of the ceramic layer was carried out to the last by the atmospheric-air plasma metal spray approach. Sample Except for having carried out thermal spraying of the interlayer by the low voltage plasma metal spray method in No.2 The test specimen was produced in the same way as No.1. Sample Except for having changed an interlayer's construction material in No.3 The test specimen was produced in the same way as No.1. Sample No.4 are the conventional thermal barrier coating and they were produced in the way same as comparison material as No.1. To the last, it is a sample. In order to raise the bond strength of the thermal barrier coating of No.1- No.4, 1000 degree-Cx 2 hours (heat treatment among a vacuum) were carried out as diffusion heat treatment.

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[0015]

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[A table 2]

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The explanation sectional view of the thermal-barrier-coating film of one example of this invention.

[Drawing 2] The conventional thermal-barrier-coating film is an explanation sectional view [ like ] 1 voice.

[Drawing 3] The explanation sectional view of other modes of the conventional thermal-barrier-coating film.

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(71) 出願人 000006208

三菱重工業株式会社

東京都千代田区丸の内二丁目5番1号

(72) 発明者 河合 久孝

兵庫県高砂市荒井町新浜二丁目1番1号

三菱重工業株式会社高砂研究所内

(72) 発明者 今津 孝幸

兵庫県高砂市荒井町新浜二丁目1番1号

三菱重工業株式会社高砂研究所内

(72) 発明者 蟹川 昌也

兵庫県高砂市荒井町新浜二丁目1番1号

三菱重工業株式会社高砂研究所内

(74) 代理人 弁理士 内田 明 (外2名)

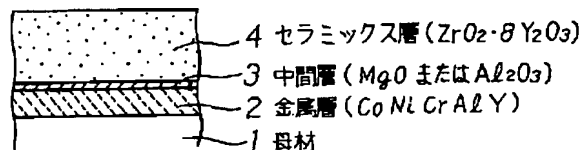
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(54) 【発明の名称】 遮熱コーティング膜

(57) 【要約】

【目的】 高温部品用の遮熱コーティング膜に関する。

【構成】 母材表面上に順次密着して設けられてなる積層膜であって、母材側から耐食・耐酸化性の高い金属層、緻密で酸素導伝性のない中間層及び遮熱性に富むセラミックス層からなる遮熱コーティング膜。





## 【特許請求の範囲】

【請求項1】 母材表面上に順次密着して設けられてなる積層膜であって、母材側から耐食・耐酸化性の高い金属層、緻密で酸素導伝性のない中間層及び遮熱性に富むセラミックス層からなることを特徴とする遮熱コーティング膜。

## 【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は遮熱コーティング膜に関し、特にガスタービンのタービン動・静翼及び燃焼器（内筒、尾筒）に有利に適用される遮熱コーティング膜に関する。

【0002】

【従来の技術】 従来技術によるガスタービン高温部品（タービン動翼・静翼、燃焼器）用遮熱コーティング膜は図2及び図3に示すような構造になっている。すなわち、図2に示すように、母材1に金属層2及びセラミックス層4が積層されているか、あるいは図3に示すように、母材1に金属層2、金属-セラミックス混合層5及びセラミックス層4が形成された多層構造である。何れの遮熱コーティング膜においても最外層はセラミックス層4よりなっている。

【0003】 これらの遮熱コーティングにおいて、金属層2は主に母材1とセラミックス層4あるいは母材1と金属セラミックス混合層5との熱膨張率の差を小さくし、これにより熱応力の緩和を図り、セラミックス層4の剥離を防ぐためのものである。また、金属-セラミックス混合層5についても、金属層2の役割りを一層積極的に狙ったものである。なお、この金属層2には、高温での耐食・耐酸化性に優れたMCrAlY合金系（M：Ni, Co, Feなどの一種以上の元素）が一般に使用されている。また、セラミックス層4は遮熱を目的とし、熱伝導率が低く、輻射率の高いZrO<sub>2</sub>系セラミックス（ZrO<sub>2</sub>・MgO, ZrO<sub>2</sub>・Y<sub>2</sub>O<sub>3</sub>など）が主に使用されている。

【0004】

【発明が解決しようとする課題】 近年ガスタービンは高効率化のため、タービン入口ガス温度の高温化が進んでいる。これに伴ない、遮熱コーティング膜はガスタービンの高温部品のメタル温度低減に非常に有効であるため、燃焼器内筒の他にガスタービン高温部品の中でも使用条件に厳しいタービン静翼、燃焼器尾筒に適用されつゝあり、さらにより使用条件の厳しいタービン動翼への適用が期待されている。

【0005】 遮熱コーティングの損傷形態として、①遮熱コーティングの構成層と母材との熱膨張差、温度差に起因する熱応力によるセラミックス層の剥離、②金属層が酸素（セラミックス層は一般にポーラスであり、これを通過して来た酸素）存在下で高温にさらされることに起因する酸化により膨張し、金属層のセラミックス層近

傍での剥離、③腐食性成分（S, Na, Vなど）による金属層、セラミックス層の腐食、④飛来微粒子に起因するエロージョンによるセラミックス層の損耗がある。タービン入口ガス温度の高温化に伴ない、遮熱コーティングが受ける熱負荷が一段と高くなり、最も問題となる遮熱コーティングの損傷形態は上述の②である。すなわち、耐酸化性に優れた金属層を用いているが、酸素存在下でより高温にさらされ、金属層が酸化するため、これがセラミックス層の剥離に連がり、遮熱コーティングの寿命が短くなるという問題が生ずる。

【0006】 本発明は上述の事情を鑑み、この問題を解決する遮熱コーティング膜を提供しようとするものである。

【0007】

【課題を解決するための手段】 本発明は母材表面上に順次密着して設けられてなる積層膜であって、母材側から耐食、耐酸化性の高い金属層、緻密で酸素導伝性のない中間層及び遮熱性に富むセラミックス層からなることを特徴とする遮熱コーティング膜である。

【0008】 本発明において、耐食・耐酸化性の高い金属層としてはMCrAlY（Y：Ni, Co, Feなどの一種以上の元素）が、緻密で酸素導伝性のない中間層としては熱膨張係数が前記金属層と後記の遮熱性に富むセラミックス層の中間のもので、MgO, CaO, CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>などが、また遮熱性に富むセラミックス層としてはZrO<sub>2</sub>・MgO, ZrO<sub>2</sub>・Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>・CeO<sub>2</sub>などのZrO<sub>2</sub>系セラミックスが用いられる。

【0009】

【作用】 本発明の遮熱コーティング膜は中間に酸素の侵入を防止する中間層が存在するため金属層が酸化されず、また、最外層のセラミックス層の剥離が生ぜず遮熱コーティング膜の寿命が長くなる。

【0010】

【実施例】 本発明の遮熱コーティング膜の一実施例を図1によって説明する。図1に示すように、母材1の上に順に耐食・耐酸化性の高い金属層2、酸素の侵入を防止する中間層3、最外層として遮熱特性の高いセラミックス層4が積層された多層構造を有している。

【0011】 金属層2用溶射材にはCoNiCrAlY（Co-32Ni-21Cr-3Al-0.5Y）を、セラミックス層4用の溶射材にはZrO<sub>2</sub>・8Y<sub>2</sub>O<sub>3</sub>を用い、中間層3用の溶射材あるいはコーティング材にはMgOあるいはAl<sub>2</sub>O<sub>3</sub>を用いた。

【0012】 表1に示す4種類の供試材を上記の溶射材あるいはコーティング材を用いて作製した。まず、試料No. 1では母材1である耐熱合金（Co基合金：30×50×3mm）の表面をAl<sub>2</sub>O<sub>3</sub>粒でグリッドプラス処理を施し、耐熱合金表面をプラズマ溶射に適した状態にした。次に、耐食・耐酸化性の高い金属層を低圧ブ

ラズマ溶射法により溶射した。その上に、中間層を電子ビーム物理蒸着法によりコーティングし、最後にセラミックス層を大気プラズマ溶射方法により溶射した。試料 No. 2 では、中間層を低圧プラズマ溶射法により溶射した以外は No. 1 と同じ要領で供試材を作製した。試料 No. 3 では、中間層の材質を変えた以外は No. 1 と同じ要領で供試材を作製した。試料 No. 4 は従来の遮熱コーティングであり、比較材として、No. 1 と同じ要領で作製した。最後に、試料 No. 1 ~ No. 4 の遮熱コーティングの付着強度を向上させるために、拡散熱処理として  $1000^{\circ}\text{C} \times 2$  時間 (真空中熱処理) を実施した。

【0013】 上述の供試材を用いて、大気電気炉中加熱 ( $1050^{\circ}\text{C} \times 300$  時間) による酸化試験を実施した。加熱後、断面マイクロ組織を観察し、金属層の耐酸化\*

\*性を評価した。次に、熱サイクル試験 ( $950^{\circ}\text{C}$  と  $200^{\circ}\text{C}$  の間の繰返し) を加熱前材及び大気電気炉中加熱 ( $1050^{\circ}\text{C} \times 300$  時間) 後材について実施した。耐剥離性は熱サイクル試験により遮熱コーティング層の剥離が生ずるまでの熱サイクル数により評価した。これらの試験結果を表2に示す。

【0014】 表2より、本発明の遮熱コーティング膜は従来のそれに比較して金属層の酸化が少ない、また、このため、加熱材の熱サイクル試験による剥離までの繰返し数が多く、本発明の遮熱コーティング膜の効果が立証された。

【0015】

【表1】

表 1

試料 No.	構 成	材 質	施工法*	膜厚(mm)
1 (本発明材)	セラミックス層	$\text{ZrO}_2 \cdot 8\text{Y}_2\text{O}_3$	APS	0.3
	中 間 層	$\text{MgO}$	EB・PVD	0.02
	金 属 層	$\text{CoNiCrAlY}$	LPPS	0.1
2 (本発明材)	セラミックス層	$\text{ZrO}_2 \cdot 8\text{Y}_2\text{O}_3$	APS	0.3
	中 間 層	$\text{MgO}$	LPPS	0.04
	金 属 層	$\text{CoNiCrAlY}$	LPPS	0.1
3 (本発明材)	セラミックス層	$\text{ZrO}_2 \cdot 8\text{Y}_2\text{O}_3$	APS	0.3
	中 間 層	$\text{Al}_2\text{O}_3$	EB・PVD	0.02
	金 属 層	$\text{CoNiCrAlY}$	LPPS	0.1
4 (比較材)	セラミックス層	$\text{ZrO}_2 \cdot 8\text{Y}_2\text{O}_3$	APS	0.3
	金 属 層	$\text{CoNiCrAlY}$	LPPS	0.1

\* APS      大気プラズマ溶射法  
LPPS      低圧プラズマ溶射法  
EB・PVD    電子ビーム物理蒸着法

【0016】

【表2】

表 2

試料 No. 1	酸化試験	熱サイクル試験	
		加熱前	加熱後
1. (本発明材)	少ない	500回以上	500回以上
2. (本発明材)	少ない	500回以上	500回以上
3. (本発明材)	少ない	500回以上	450回で剥離
4. (比較材)	多い	500回以上	275回で剥離

## 【0017】

【発明の効果】本発明の遮熱コーティング膜はセラミックス層と金属層との間に中間層を設け、この中間層により酸素の通過が防止されるので、金属層の酸化が生じにくく、遮熱コーティング膜の寿命が向上する。したがって、本発明による遮熱コーティング膜をガスタービンに適用することにより、より入口ガス温度が高い厳しい使用環境、あるいはより長時間の使用に耐えるガスタービン高温部品（タービン動・静翼、燃焼器内筒・尾筒）を

提供することができる。

## 【図面の簡単な説明】

【図1】本発明の一実施例の遮熱コーティング膜の説明断面図。

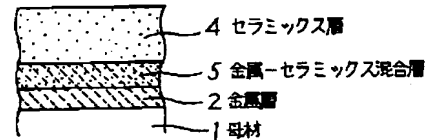
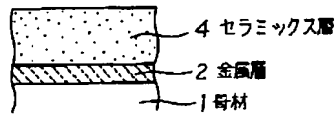
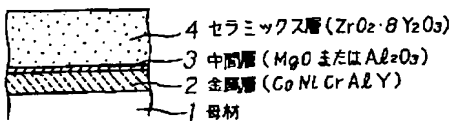
【図2】従来の遮熱コーティング膜の一態様の説明断面図。

【図3】従来の遮熱コーティング膜の他の態様の説明断面図。

【図1】

【図2】

【図3】



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(72)発明者 北井 敬人

兵庫県高砂市荒井町新浜二丁目1番1号  
三菱重工業株式会社高砂製作所内

(72)発明者 広田 法秀

兵庫県高砂市荒井町新浜二丁目1番1号  
三菱重工業株式会社高砂製作所内